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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a battery having the high capacity, excellent in charging and discharging cycle characteristics, and having the small quantity metal used by making a negative electrode of a mixed system of a conductive auxiliary material of carbon grains having metal for making alloy with lithium and graphite capable of being intercalated and de-intercalated, and making the grain diameter of carbon grains having metallic particles smaller than the grain diameter of graphite.
SOLUTION: A negative electrode is preferably a mixed system of a conductive auxiliary material of carbon grains having metal for forming alloy with lithium and amorphous carbon, and metal in the conductive auxiliary material is selected from Al, Sb, B, Ba, Bi, Cd, Ca, Ga, In, Ir, Pd, Pb, Hg, Si, Ag, Sr, Te, Ti and Sn. It is desirable that the specific surface area of the carbon grain is in the range of 1 to 1000 m2/g and that the grain diameter of metallic particles is 500 nm or less. Therefore, the service capacity is increased, electric conductivity is improved, the output density is increased, cycle characteristics are improved, and heat radiation property is improved.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to the negative electrode for lithium secondary batteries which discharge capacity and whose power density are size and was excellent in the cycle property with respect to a lithium secondary battery. It is related with amelioration of the cell which was made to come to hold mixed stock with the graphite particle and amorphous carbon which make the carbon particle which supported the metal which forms an alloy by seven or less atomic ratio especially to the lithium atom 1 electric conduction assistant **, and can intercalate and deintercalate Li ion to a charge collector, and used this for the negative electrode.

[0002]
[Description of the Prior Art] As a negative electrode of a lithium secondary battery, although alloys, such as the (Li) metal and Li-aluminum, and Li-Pb, had been used conventionally, these cells had the short short circuit and cycle life of positive/negative two poles by deposit of a resin-like lithium, and had the defect that energy density was low. In order to solve these troubles recently, the research which uses carbon material for a negative electrode is active. This kind of negative electrode is indicated by for example, a publication-number No. 299073 [five to] official report and a publication-number No. 121258 [two to] official report.
[0003] The configuration in JP,5-299073,A is using as the electrode material the carbon complex which consists of covering with the film containing a VIII group's metallic element the surface of the high crystal carbon particle which forms the heart, and carbon covering a it top further, and since the surface area of an electrode is large, it supposes that charge-and-discharge capacity and charge-and-discharge speed improved remarkably, at the same time the carbon material which has surface random layer structure by this helps the intercalation of a lithium.
[0004] On the other hand, in JP,2-121258,A, it is hexagonal and the charge-and-discharge cycle life is made it is long and good [the charge-and-discharge property in a high current] by considering as the mixture of the carbon material and Li which are $H/C < 0.15$ and spacing> 0.337nm and magnitude Lc<15nm of the microcrystal of C shaft orientations, and the metal in which an alloy is possible.
[0005] However, in any, neither composite difficulty [negative-electrode carbon material] nor carbonaceous geometric capacity was pulled out, and it was not able to be said that power density was still enough. Furthermore, metal support carbon had the problem said that cost is high depending on a metaled price.
[0006]
[Problem(s) to be Solved by the Invention] As mentioned above, when carbon material and composite are used as a negative electrode, there is a problem in respect of that carbonaceous geometric capacity cannot be pulled out, the difficulty of electrode manufacture, or cost.
[0007] The purpose of this invention is by using for a negative electrode by making into electric conduction assistant ** the carbon particle which supported the very fine particle of the metal in which a lithium and an alloy are possible for a charge-and-discharge cycle property to be excellent in high capacity, and offer a lithium secondary battery with little amount of the metal used.
[0008]
[Means for Solving the Problem] this invention persons came to complete this invention based on knowledge expressed below, as a result of examining many things, in order to solve the above-mentioned trouble.
[0009] Drawing 5 shows a measurement result of cycle property B1' of a conventional-type negative electrode and an advanced negative electrode of this invention, and A1'. Used carbon is the natural graphite which carried out high grade-ized processing, and particle size is about 11 micrometers. A paste with which it was made for carbon and PVDF to become the weight ratio of 90:10 to this carbon using a solution which dissolved polyvinylidene fluoride (it outlines Following PVDF) in N-methyl pyrrolidone (it outlines Following NMP) as a binder was applied to copper foil with a thickness of 20 micrometers which is a charge collector.
[0010] An advanced negative electrode was created in the following procedures. Suspension of the 9.0g of a natural graphite (particle size of 11 micrometers) which carried out high grade-ized processing is carried out to 450ml of water containing 25ml ethyl alcohol. A 1.73g silver nitrate ($AgNO_3$) is dissolved warming and strong-stirring this at about 60 degrees C. 0.5% of the weight of a sodium-tetrahydroborate ($NaBH_4$) aqueous solution is dropped at this with a micro tube pump, and a reduction reaction is completed over about 4 hours or more. Then, it filtered and rinsed and the vacuum drying was carried out at 300 degrees C for 6 hours.
[0011] According to the chemical analysis, the amounts of support of the obtained powder A were 9.9 % of the weight and the good amount of support to 10.0% of the weight of a preparation presentation. Moreover, when an X diffraction investigated an Ag's existence condition, only a diffraction line of silver of a metal condition was detected. Next, by energy dispersion mold electron probe microanalysis, when a distributed condition of Ag was observed, Ag particle was distributed over a front face of a graphite particle, and was condensed a little in the end-face section of a graphite particle. When magnitude of Ag particle was furthermore observed with a transmission electron microscope, particle several 100nm or less was distributing to homogeneity mostly. This carbon material was applied to Cu foil by the same method as the above-mentioned.
[0012] After carrying out the vacuum drying of both at 80 degrees C after an air dried for 2 hours and fabricating them by pressure of 0.5 ton/cm2, the vacuum drying was carried out at 120 more degrees C for 3 hours, and it considered as a negative electrode, respectively. A micropore film made from polyethylene which is a separator about one of the negative electrodes of these is inserted in between, and it is 1M as a counter electrode of a lithium metal, combination, and the electrolytic solution. A trial cel using a lithium metal as $LiPF_6$/ethylene

carbonate dimethyl carbonate (it is written as EC-DMC below) and a reference pole was assembled. Charge-and-discharge speed performed [about a conventional-type negative electrode and an advanced negative electrode] a cycle trial using this trial cel by potential width-of-face:0.01-1.0V of 120mA per carbon 1g, and charge and discharge, respectively.

[0013] When a conventional-type negative electrode was used by result of a trial so that clearly from drawing 5 , discharge capacity fell for every cycle and discharge capacity fell to about 60% of initial capacity after about 500 cycles. when the advanced negative electrode 2 is used, in order, as for an early discharge capacity, to, add alloying capacity of Ag and Li on the other hand -- a carbonaceous negative electrode -- receiving -- about 30 mAh/cm3 -- it was large and, as for a decreasing rate, an effect of an advanced negative electrode was regarded as 4.5 (%) very small after 500 cycles in life. An improvement of this cycle property is considered with since it controlled falling for bulging of an electrode with which the current collection effect between carbonaceous particles originates in a volume change by repeat of charge and discharge etc. with a metal support carbon negative electrode.

[0014] It is a factor important for improvement in discharge capacity or a cycle property to raise the current collection nature of a negative-electrode binder layer from the above result, and alloying capacity with a lithium found out bringing about a function in which it can use and improvement in electrical conductivity by making a metal intervene between carbon particles or thermal conductivity etc. can be expected by supporting a metaled very fine particle on carbon.

[0015] A summary of this invention is described how. That is, it is the lithium secondary battery characterized by a carbon particle which supported a metal with which said negative electrode forms an alloy by seven or less atomic ratio to the lithium atom 1 in a lithium secondary battery equipped with the electrolytic solution with which the 1st invention is immersed in a positive electrode of a pair and a negative electrode, a separator that intervenes among positive/negative two poles, and positive/negative two poles and a separator being electric conduction assistant **.

[0016] It is the lithium secondary battery characterized by being the mixed stock of carbon particle electric conduction assistant ** which supported a metal with which said negative electrode forms an alloy by seven or less atomic ratio to the lithium atom 1 in a lithium secondary battery equipped with the electrolytic solution with which the 2nd invention is immersed in a positive electrode of a pair and a negative electrode, a separator that intervenes among positive/negative two poles, and positive/negative two poles and a separator, and a graphite which can intercalate Li ion and can be deintercalated.

[0017] It is the lithium secondary battery characterized by the 3rd invention being the mixed stock of carbon particle electric conduction assistant ** and amorphous carbon which supported a metal with which a negative electrode forms an alloy by seven or less atomic ratio to the lithium atom 1.

[0018] A metal which supports the 4th invention to electric conduction assistant ** is a lithium secondary battery characterized by using at least one kind in aluminum, Sb, B, Ba, Bi, Cd, calcium, Ga, In, Ir, Pd, Pb, Hg, Si, Ag, Sr, Te, Tl, and Sn.

[0019] The 5th invention is a lithium secondary battery characterized by for specific surface area of said carbon particle being 1-1000m2/g, and particle size of support metal particles being 500nm or less.

[0020] A negative electrode makes it come to hold [invention / 6th] mixed stock of carbon particle electric conduction assistant ** which supported a metal which forms an alloy by seven or less atomic ratio to the lithium atom 1, and a graphite particle which can intercalate and deintercalate Li ion to a charge collector. Said graphite particle is a lithium secondary battery characterized by for a spacing (d002) by X-ray diffraction method being 0.3354-0.3369nm, and for magnitude (Lc) of a crystal of C shaft orientations being 30nm or more, and specific surface area being 0.1-30m2/g.

[0021] A spacing (d002) a negative electrode makes it come to hold [invention / 7th] mixed stock of a carbon particle electric conduction assistant ** and an amorphous carbon particle which supported a metal which forms an alloy by seven or less atomic ratio to the lithium atom 1 to a charge collector, and according [said amorphous carbon particle] to an X-ray diffraction method is the lithium secondary battery characterized by being 0.337nm or more.

[0022] It is the lithium secondary battery characterized by for positive-electrode material being LiXO2 or LiX 2O4 (X being a kind of transition metals, such as Co, nickel, and Mn, or two or more sorts), and the presentation ratio having superfluous Li to a SUTOIKIO presentation in a cell with which the 8th invention combined a negative electrode, a positive electrode, and the electrolytic solution.

[0023] It is the lithium secondary battery with which 9th invention is characterized by electrolytic-solution layers being copolymer electrolytes, such as poly vinylidene fluoride and hexafluoropropylene.

[0024] It is the lithium secondary battery which the 10th invention intervenes a separator between a positive electrode and a negative electrode, and said negative electrode covers a mixolimnion to a conductive member, consists of a graphite which can intercalate and deintercalate Li ion, and Li and a carbon particle which has metal particles which form an alloy in a lithium secondary battery immerse with the electrolytic solution in positive/negative two poles and a separator, and is characterize by the amount of metal particles in this mixolimnion be more than 1 weight (%).

[0025] Weight [one to 5] (%) The amount of metal particles in which the 11th invention forms Li and an alloy in the above-mentioned mixolimnion is a lithium secondary battery according to claim 10 characterized by having.

[0026] The 12th invention is a lithium secondary battery according to claim 10 characterized by being small and constituting particle size of a carbon particle which supported metal particles from particle size of a graphite.

[0027] Carbon which supports a metal as electric conduction assistant ** of this invention heat-treats a ******** material obtained from a high crystallinity carbon particle, for example, a natural graphite, petroleum coke, or coal pitch coke at an elevated temperature 2500 degrees C or more as a graphite which can intercalate amorphous carbon and Li ion which have high specific surface area, and can be deintercalated, and is obtained. 0.1-20 micrometers 50 micrometers or less are preferably suitable for mean particle diameter of these amorphous carbon and a graphite. Moreover, configurations may be the shape of a globular form, massive, and a piece of phosphorus, fibrous, or those grinding articles.

[0028] Next, as a support metal, although a kind is chosen at least among aluminum, Sb, B, Ba, Bi, Cd, calcium, Ga, In, Ir, Pd, Pb, Hg, Si, Ag, Sr, Te, Tl, and Sn, an element which fulfills the following conditions is desirable.

[0029] (1) an alloy presentation with many lithium contents, and (2) atomic weights -- comparatively -- small -- (6) with few problems on (5) abandonment with a low oxidation-reduction potential of ease [(3) reduction with comparatively large density], and (4) lithium alloy -- it is comparatively cheap.

[0030] What is necessary is just to apply the optimal supporting method as the metaled support method, corresponding to a metal kind to be used, although there are methods, such as vacuum deposition, the sputtering method, a wet reduction method, electrochemistry reduction, plating, and a gaseous-phase reducing gas approach. moreover -- as the metaled amount of support -- 10-50 -- wt (%) -- desirable -- 10-30 -

- wt (%) is the optimal. Furthermore, when particle size of a supported metal takes into consideration a deposit and a dissolution rate of a lithium alloy in charge and discharge, metal particles are small as much as possible, and its 500nm or less is desirable as conditions with which it is expected that the particle is more advantageous to reinforcement considering decay of metal particles accompanying a volume change of alloying, and these are filled.

[0031] Although a negative electrode is created using a graphite which can intercalate a metal support carbon particle and Li ion which were obtained above, and can be deintercalated, a binder is used in this case. As a binder, if it does not react, for example with the electrolytic solutions, such as EPDM (ethylene-propylene terpolymer), PVDF, and polytetrafluoroethylene, it will not be limited especially. loadings of a binder -- carbon -- receiving -- 1-30 -- wt (%) -- desirable -- 5-15 -- wt (%) is suitable. It is possible to fill up the shape of a film and a foam metal and to fit a cell configuration on the shape of the shape of a sheet and a film and a metallic foil, as a negative-electrode configuration using the above-mentioned mixture. Binder layer thickness has the desirable range of 10-200 micrometers.

[0032] Thus, an obtained negative electrode can be used as optimal lithium secondary battery by combining with a positive electrode, a separator, and the electrolytic solution which are usually used. A multiple oxide expressed with a general formula LiXO2 or LiX 2O4 (X is a kind of transition metals, such as Co, nickel, and Mn, or two or more sorts) as an active material used for a positive electrode, For example, a SUTOIKIO presentation of a multiple oxide containing lithiums, such as LiCoO2, LiNiO2, LiMnO2, Li(nickel1-xCox) O2, and LiMn 2O4, and 2OLiMn4 compound is received. What has superfluous Li may be used, what mixed carbon black, carbon, and a binder of an electric conduction agent to this is applied to charge collectors, such as aluminum foil, and it considers as a positive electrode.

[0033] As a separator, porous membrane of polypropylene, polyethylene, or a polyolefine system is used. Moreover, as the electrolytic solution, two or more kinds of mixed solvents, such as propylene carbonate (PC), ethylene carbonate (EC), 1, 2-JIMETOKISHI ethane (DME), JIMECHIRU carbonate (DMC), JIECHIRU carbonate (DEC), and metier chill carbonate (MEC), are used. Moreover, as an electrolyte, there are LiPF6, LiBF4, and LiClO4 grade, and what was dissolved in the above-mentioned solvent is used. Moreover, a polymer electrolyte which has a function of a separator, the electrolytic solution, and an electrolyte may be used.

[0034] Intercalation of carbon particle electric conduction assistant ** and Li ion which supported a metal which is and forms an alloy for a carbon negative electrode by seven or less atomic ratio to the lithium atom 1 a lithium secondary battery by the above configuration -- By improving to mixed stock with a graphite and amorphous carbon which can be deintercalated, increase of (1) discharge capacity, (2) Reduction of improvement in electrical conductivity, (3) power density, (4) cycle property, and heat leakage nature in (5) group cells and (6) high-speed charge and discharge, and the amount of (7) support metals was attained.

[0035]

[Embodiment of the Invention] (Example 1) Suspension of the 8.0g of acetylene black (specific surface area: 70m2/g) is carried out to 1800ml of water containing the ethyl alcohol of 20vol(%). A 3.15g silver nitrate (AgNO3) is dissolved warming and strong-stirring this at about 50 degrees C. The sodium-tetrahydroborate (NaBH4) aqueous solution of 2.0 weight (%) is dropped at this with a micro tube pump, and a reduction reaction is completed over 4 hours.

[0036] Then, it filtered and rinsed and the vacuum drying was carried out at 150 degrees C for 6 hours. According to the chemical analysis, the amounts of support of the obtained powder A were 19.8 weight (%) and the good amount of support to the 20.0 (%) weight of a preparation presentation. Moreover, when the X diffraction investigated the Ag's existence condition, only the diffraction line of the silver of a metal condition was detected.

[0037] Next, by energy dispersion mold electron probe microanalysis, when the distributed condition of Ag was observed, Ag particle was distributed over the front face of acetylene black. When the magnitude of Ag particle was furthermore observed with the transmission electron microscope, the particle 500nm or less was distributing to homogeneity mostly.

[0038] (Example 2) Suspension of the 8.0g of carbon black (specific surface area: 600m2/g) is carried out to 1800ml of water containing the ethyl alcohol of 20vol(%). A 3.15g silver nitrate (AgNO3) is dissolved warming and strong-stirring this at about 50 degrees C. The sodium-tetrahydroborate (NaBH4) aqueous solution of 2.0 weight (%) is dropped at this with a micro tube pump, and a reduction reaction is completed over 4 hours.

[0039] Then, it filtered and rinsed and the vacuum drying was carried out at 150 degrees C for 6 hours. According to the chemical analysis, the amounts of support of the obtained powder B were 19.8 weight (%) and the good amount of support to the 20.0 (%) weight of a preparation presentation. Moreover, when the X diffraction investigated the Ag's existence condition, only the diffraction line of the silver of a metal condition was detected. Next, by energy dispersion mold electron probe microanalysis, when the distributed condition of Ag was observed, Ag particle was distributed over the front face of a graphite particle. When the magnitude of Ag particle was furthermore observed with the transmission electron microscope, the particle 500nm or less was distributing to homogeneity mostly.

[0040] The spacing (d002) by Powder A and the X-ray diffraction method which were acquired with the gestalt 1 of the above-mentioned implementation (Example 3) By 0.336nm The graphite whose specific surface area the magnitude (Lc) of the crystal of C shaft orientations is 100nm, and is 3.2m2/g is mixed to (1:9) by the weight ratio. Use N-methyl pyrrolidone solution of PVDF for this as a binder, and the paste mixed powder and PVDF were made to become the weight ratio of 90:10 is applied to copper foil with a thickness of 20 micrometers which is a charge collector. After an air dried and after carrying out the vacuum drying at 80 degrees C for 3 hours and fabricating by the pressure of 0.5 ton/cm2, the vacuum drying was carried out at 120 more degrees C for 2 hours, and the negative electrode was obtained. It combined with the counter electrode of a lithium metal on both sides of these negative electrodes and polyethylene film production, and the trial cel which used 1MliPF6/EC-DMC for the electrolytic solution, and used the lithium metal for the reference pole was assembled. Charge and discharge current density set 0.3 - 4.0 mA/cm2 and bound potential of charge and discharge to 1.0V and 0.01V, respectively.

[0041] The result was shown in drawing 6 as compared with the graphite negative electrode which consists of the negative electrode and this invention of only a graphite. In drawing 6 , a horizontal axis is expressed with discharge current density, and the axis of ordinate is expressed with the discharge capacity maintenance factor (%). clearer than drawing -- as -- current density -- 1 mA/cm2 -- until -- although a difference is not seen in the negative electrode of this invention and the conventional technology, it turns out that there are few discharge capacity maintenance-factor falls of the discharge property A1 which used the negative electrode which consists of the carbon material which supported Ag of this invention from the hit exceeding 1 mA/cm2 to the capacity of the discharge property B1 of the conventional technology which used the negative electrode of only a graphite falling remarkably, and a graphite. The amount of Ag in this invention negative electrode is 2wt(%) to activity section mass. When the powder B incidentally obtained with the gestalt 2 of operation performed the same trial as Powder A, the almost same result was obtained.

[0042] The spacing (d002) by Powder A and the X-ray diffraction method which were acquired with the gestalt 1 of the above-mentioned implementation (Example 4) By 0.336nm Are a weight ratio (5:95) and (15:85) the graphite whose specific surface area the magnitude (Lc)

of the crystal of C shaft orientations is 100nm, and is 3.2m2/g is mixed. Use N-methyl pyrrolidone solution of PVDF for this as a binder, and the paste mixed powder and PVDF were made to become the weight ratio of 90:10 is applied to copper foil with a thickness of 20 micrometers which is a charge collector. After an air dried and after carrying out the vacuum drying at 80 degrees C for 3 hours and fabricating by the pressure of 0.5 ton/cm2, the vacuum drying was carried out at 120 more degrees C for 2 hours, and the negative electrode was obtained.

[0043] When the same trial as an example 3 was performed using these negative electrodes, the almost same value as drawing 6 was shown. Incidentally in the case of (5:95), the amount of Ag used is equivalent to 3wt(%) by 1wt(%) and (15:85).

[0044] The spacing (d002) by Powder A and the X-ray diffraction method which were acquired with the above-mentioned gestalt 1 (Example 5) By 0.382nm And the amorphous carbon whose specific surface area is 4.5m2/g is mixed to (1:9) by the weight ratio. Use N-methyl pyrrolidone solution of PVDF for this as a binder, and the paste mixed powder and PVDF were made to become the weight ratio of 90:10 is applied to copper foil with a thickness of 20 micrometers which is a charge collector. After an air dried and after carrying out the vacuum drying at 80 degrees C for 3 hours and fabricating by the pressure of 2.0 ton/cm2, the vacuum drying was carried out at 120 more degrees C for 2 hours, and the negative electrode was obtained.

[0045] It combined with the counter electrode of a lithium metal on both sides of these negative electrodes and polyethylene film production, and the trial cel which used 1MliPF6/PC-DMC for the electrolytic solution, and used the lithium metal for the reference pole was assembled. Charge and discharge current density set 0.3 - 4.0 mA/cm2 and bound potential of charge and discharge to 1.5V and 0.005V, respectively. moreover, charge -- 4h CCCV -- it carried out by law. In order to compare, the trial with the same said of the negative electrode of only amorphous carbon was performed. Consequently, it has checked that there were few discharge capacity maintenance-factor falls of the negative electrode which mixed Ag support carbon material which consists of the hit which exceeds 2 mA/cm2 like an example 3 by this invention to the capacity of the negative electrode of only amorphous carbon falling remarkably, and amorphous carbon.

[0046] (Example 6) Suspension of the 8.0g of acetylene black (specific surface area: 70 m2/g) is carried out to 1800ml of water containing the ethyl alcohol of 20vol(%). The solution made to dissolve 3.8gSnCl(s)22H2O in 2mlCH3COOH+200mlC2H5OH is added warming and strong-stirring this at about 50 degrees C. The sodium-tetrahydroborate (NaBH4) aqueous solution of 2.0 weight (%) is dropped at this with a micro tube pump, and a reduction reaction is completed over 4 hours.

[0047] Then, it filtered and rinsed and the vacuum drying was carried out at 150 degrees C for 6 hours. Reduction processing was performed for the obtained powder C at 400 degrees C among the 1(%) H2-/helium air current for 5 hours. When the chemical analysis of Powder C was carried out, they were 19.7 weight (%) and the good amount of support to the 20.0 (%) weight of a preparation presentation. Moreover, when the X diffraction investigated the Sn's existence condition, the diffraction line of a ****** minute amount was detected by Sn and SnO2 of a metal condition. Next, by energy dispersion mold electron probe microanalysis, when the distributed condition of Sn was observed, Sn particle was distributed over the front face of acetylene black. When the magnitude of Sn particle was furthermore observed with the transmission electron microscope, the particle 500nm or less was distributing to homogeneity mostly.

[0048] The spacing (d002) by Powder C and the X-ray diffraction method which were acquired with the gestalt 6 of the above-mentioned implementation (Example 7) By 0.336nm The graphite whose specific surface area the magnitude (Lc) of the crystal of C shaft orientations is 100nm, and is 3.2m2/g is mixed to (1:9) by the weight ratio. Use N-methyl pyrrolidone solution of PVDF for this as a binder, and the paste mixed powder and PVDF were made to become the weight ratio of 90:10 is applied to copper foil with a thickness of 20 micrometers which is a charge collector. After an air dried and after carrying out the vacuum drying at 80 degrees C for 3 hours and fabricating by the pressure of 0.5 ton/cm2, the vacuum drying was carried out at 120 more degrees C for 2 hours, and the negative electrode was obtained. The same trial as an example 3 was performed using these negative electrodes. Consequently, the discharge capacity maintenance factor [in / in current density / 2 mA/cm2] was the value of 95 (%).

[0049] The spacing (d002) by Powder C and the X-ray diffraction method which were acquired with the gestalt 6 of the above-mentioned implementation (Example 8) By 0.382nm And the amorphous carbon whose specific surface area is 4.5m2/g is mixed to (1:9) by the weight ratio. Use N-methyl pyrrolidone solution of PVDF for this as a binder, and the paste mixed powder and PVDF were made to become the weight ratio of 90:10 is applied to copper foil with a thickness of 20 micrometers which is a charge collector. After an air dried and after carrying out the vacuum drying at 80 degrees C for 3 hours and fabricating by the pressure of 2.0 ton/cm2, the vacuum drying was carried out at 120 more degrees C for 2 hours, and the negative electrode was obtained.

[0050] It combined with the counter electrode of a lithium metal on both sides of these negative electrodes and polyethylene film production, and the trial cel which used 1MliPF6/PC-DMC for the electrolytic solution, and used the lithium metal for the reference pole was assembled. Charge and discharge current density set 0.3 - 4.0 mA/cm2 and bound potential of charge and discharge to 1.5V and 0.005V, respectively. moreover, charge -- 4h CCCV -- it carried out by law. As for the negative electrode which mixed Sn support carbon material which changes by this invention, and amorphous carbon, the current density of the discharge capacity maintenance factor in 2 mA/cm2 was the value of 93 (%).

[0051] (Example 9) This example describes the configuration of the cell combined with the negative electrode, the positive electrode, and the electrolytic solution which were obtained with the gestalt 1 of operation.

[0052] the mixture which set it as the artificial graphite as LiCoO2 and an electric conduction agent, and set polyvinylidene fluoride to 87:9:4 by the weight ratio as a binder as positive active material -- the slurry was used as aluminum foil which is a charge collector with ******, and was dried and rolled out, and the positive electrode was created.

[0053] As the electrolytic solution, as an electrolyte, LiPF6 was dissolved in the solvent which mixed ethylene carbonate (EC) and dimethyl carbonate (DMC) by the volume ratio 1:2 so that it might become with 1 M/l, and the electrolytic solution was obtained.

[0054] the AA using the positive electrode and the electrolytic solution of the negative electrode and the above-mentioned as a cell -- drawing 1 explains the cell of a mold.

[0055] In drawing 1 , it consists of the separator 8 of the porous membrane made from polyethylene which isolates a positive electrode 6 and a negative electrode 7, and these two poles, the negative-electrode can 9, the positive-electrode lead 10, the negative-electrode lead 11, a positive-electrode external terminal 12, an obturation gasket 13, an electric insulating plate 14, etc.

[0056] It is spirally wound through a separator 8 and a positive electrode 6 and a negative electrode 7 are contained in the negative-electrode can 9. The positive electrode 6 is connected to the positive-electrode external terminal 12 through the positive-electrode lead 10. It connects with the negative-electrode can 9 through the negative-electrode lead 11, and the negative electrode 7 enables it to take out electrical energy outside. Insulating seal is carried out between the positive-electrode external terminal 12 and the negative-electrode can 9

at the obturation gasket 13. Moreover, the base of the negative-electrode can 9 and the corresponding electric insulating plate 14 have insulated between the negative-electrode can 9, a separator 8, and positive electrodes 6. In addition, since the main component part of the carbon button mold cell of drawing 2 and the cell of drawing 1 is the same, by the carbon button mold cell, the same sign is given to the same components as the main component part of the cell of drawing 1 , and explanation is omitted.

[0057] Drawing 3 (A) and (B) explain the configuration of a negative electrode 7. Mixolimnion 7B is covered to conductive member, for example, Cu foil, 7A, and it is **. Mixolimnion 7B consists of the layer which mixed graphite 7G which can intercalate Li ion and can be deintercalated, and carbon particle 7C (electric conduction assistant ** is called below) which ****(ed), the metal very fine particle, for example, Ag7D, which forms Li and an alloy, by binder 7E. Binder 7E is graphite 7G, Ag7D, and binding material that binds carbon particle 7C.

[0058] Drawing 4 explains the mixing ratio of graphite 7G and electric conduction assistant **. In Ag, at the time of 1 weight (%), 95 weight (%) and electric conduction assistant ** consist [graphite 7G] of 5 weight (%), and, as for drawing 4 , 20 weight (%) is equivalent to Ag of 1 weight (%) among 5 weight (%). Moreover, in Ag, at the time of 5 weight (%), 75 weight (%) and electric conduction assistant ** consist [graphite 7G] of 25 weight (%), and 20 weight (%) is equivalent to Ag of 5 weight (%) among 25 weight (%).

[0059] For this reason, if it becomes below 5 weight (%) in the conventional property B which does not contain Ag so that clearly from the discharge capacity maintenance-factor property of drawing 4 , a discharge capacity maintenance factor falls rapidly and cannot use it as a cell.

[0060] However, if the property A of this invention contains Ag within the limits of 1 (%) to 5 weight (%), it can maintain the property A of a discharge capacity maintenance factor to 90 (%), but if Ag becomes below 1 weight (%), a discharge capacity maintenance factor falls rapidly and cannot use it as a cell. Moreover, since a discharge capacity maintenance factor does not change even if Ag contains more than 5 weight (%), carrying out 1 weight (%) - 5 weight (%) content can attain [that it is the most economical and] the following effects. When the content of Ag is carried out more than 15 weight (%), shortly, it becomes cost high, changes economically and is ******.

[0061] Moreover, if the particle size of carbon particle 7C (electric conduction assistant **) which ****(ed) Ag7D is smaller than the particle size of graphite 7G and being constituted Electric conduction assistant ** tends to permeate between graphite 7G and graphite 7G, and pack density (%) increases. A high current can be passed without falling rapidly, even if discharge current density mA/cm2 exceeds 1 compared with the conventional discharge property B1 that the discharge property A1 of this invention does not use electric conduction assistant ** like drawing 6 as a result of a particle comrade's point of contact increasing and a current path's increasing.

[0062] That is, drawing 5 is property drawing showing the relation of the number of cycles (time) and discharge capacity (mAh/cm3) which perform charge discharge of the lithium rechargeable battery of this invention. Although the above-mentioned negative electrode was used for the negative electrode of this invention and the conventional lithium rechargeable battery by this invention, what mixed a graphite and carbon was used for it in the conventional example. It considered as the test condition of drawing 5 , and carried out as charge-and-discharge speed:1C, charge beginning-and-the-end ******:4.2V, and discharge-final-voltage:2.5V.

[0063] Consequently, even if the number of cycles increases compared with the conventional property B1, the number of cycles does not fall, to the engine performance stabilized up to 300 cycle being obtained, if the number of cycles increases the conventional property B1, discharge capacity will fall remarkably and the engine performance will not be stabilized [the property A1 of the lithium rechargeable battery of this invention] by the property A1 of the lithium rechargeable battery of this invention. For this reason, a sound, a light, etc. which were stabilized over the long period of time could be enjoyed, without exchanging a lithium rechargeable battery frequently compared with the conventional lithium rechargeable battery, when using the lithium rechargeable battery which used the negative electrode of this invention.

[0064] Furthermore, property drawing showing the relation between a discharge capacity maintenance factor (%) and discharge current density (mA/cm2) by drawing 6 explains. Since a high current can be passed without decreasing rapidly even if discharge current density (mA/cm2) increases the discharge property A1 of this invention compared with the conventional discharge property B1, an above-mentioned effect can be attained like drawing 5 .

[0065]

[Effect of the Invention] If electric conduction assistant **, the graphite, or amorphous carbon which supported the very fine particle of the negative electrode obtained by this invention as mentioned above, i.e., the metal which forms an alloy in a carbon particle by seven or less atomic ratio to lithium 1 atom, is mixed and it uses for a negative electrode, by making a metal intervene between carbon particles, (1) electrical conductivity will improve and the speed of a charge-and-discharge reaction will improve. (2) Since discharge capacity becomes large, naturally the power density of a cell also becomes large. A cycle property can also improve along with (3) and (1), and the heat leakage nature in a group cell can also be raised. (4) The amount of the support metal used can be reduced.

[Translation done.]